Semi-empirical Approximations

The Hartree-Fock calculation is based on a mean field approximation in that each electron is only subject to the average influence of the other electrons. This is a crude approximation. The results of such calculations of molecular properties shows that the structure of molecules is, nevertheless, quite well reproduced but the energy of bonds and activation energy of transitions are not in good agreement with experimental measurements or higher level calculations. The frequency of vibrational modes is typically about 10% too high.

There are several approaches to improve on the Hartree-Fock approximation. One is the semi-empirical approach. There, the goal is to both reduce the computational effort and obtain at the same time better agreement with experimental results. The most computationally demanding integrals are approximated by simple expressions that have parameters adjusted by comparison with some set of experimental data. The two electron, four center integrals are particularly demanding with computational effort scaling as the number of basis functions, K, to the fourth power. By approximating these integrals by analytical functions fitted to reproduce experimental data, the semi-empirical methods can be applied to much larger molecules than Hartree-Fock calculations and in some cases, for the types of molecules they are fitted to, give more accurate results.

It is important to realise that application of semi-empirical approaches to molecules that are significantly different from those included in the data set they are fitted to, the results can be worse than Hartree-Fock and even unphysical. It is, therefore, important to know the range of validity of a given semi-empirical approximation. Since the computational effort is smaller than for Hartree-Fock, it can be useful to start a computational study by doing semi-empirical calculations and get a first estimate of the molecular structure, and then turn to more accurate methods. This can save computer time if the structure is not well known and the molecule is within the range of validity for the semi-empirical method. The most commonly used semi-empirical methods are MNDO, AM1 and PM3. Many calculations of large biomolecules are based on semi-empirical approximations because higher level calculations are not feasible.

For a review of semi-empirical approximations, see the link "review article on semi-empirical methods"with the article "Semiempirical Quantum Mechanical Methods for Noncovalent Interactions for Chemical and Biochemical Applications".